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(54) Title: METALLIC GLASS ALLOYS FOR MECHANICALLY RESONANT MARKER SURVEILLANCE SYSTEMS

(57) Abstract

A glassy metal alloy consists essentially of the formula: $Fe_aCo_bNi_cM_dB_eSi_fC_g$, where "M" is at least one member selected form the group consisting of molybdenum, chromium and manganese, "a-g" are in atom percent, "a" ranges from about 30 to about 45, "b" ranges form about 4 to about 40, "c" ranges from about 5 to about 45, "d" ranges from about 0 to about 3, "e" ranges from about 10 to about 25, "f" ranges from about 0 to about 15 and "g" ranges from about 0 to about 2. The alloy can be cast by rapid solidification into ribbon, annealed to enhance magnetic properties, and formed into a marker that is especially suited for use in magneto-mechanically actuated articles surveillance systems. Advantageously, the marker is characterised by relatively linear magnetization response in the frequency regime wherein harmonic marker systems operate magnetically. Voltage amplitudes detected from the marker are high, and interference between surveillance systems based on mechanical resonance and harmonic re-radiance is virtually eliminated.

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METALLIC GLASS ALLOYS FOR MECHANICALLY RESONANT MARKER SURVEILLANCE SYSTEMS

CROSS REFERENCE TO RELATED APPLICATIONS

This is a continuation-in-part of US Application Serial No.08/421,094, filed April 13, 1995 entitled Metallic Glass Alloys for Mechanically Resonant Marker Surveillance Systems.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to metallic glass alloys; and more particularly to metallic glass alloys suited for use in mechanically resonant markers of article surveillance systems.

2. Description of the Prior Art

Numerous article surveillance systems are available in the market today to help identify and/or secure various animate and inanimate objects. Identification of personnel for controlled access to limited areas, and securing articles of merchandise against pilferage are examples of purposes for which such systems are employed.

An essential component of all surveillance systems is a sensing unit or "marker", that is attached to the object to be detected. Other components of the system include a transmitter and a receiver that are suitably disposed in an "interrogation" zone. When the object carrying the marker enters the interrogation zone, the functional part of the marker responds to a signal from the transmitter, which response is detected in the receiver. The information contained in the response signal is then processed for actions appropriate to the application: denial of access, triggering of an alarm, and the like.

Several different types of markers have been disclosed and are in use. In one type, the functional portion of the marker consists of either an antenna and diode or an antenna and capacitors forming a resonant circuit. When placed in an electromagnetic field transmitted by the interrogation apparatus, the antenna-diode marker generates harmonics of the interrogation frequency in the receiving antenna. The detection of the harmonic or signal level change indicates the presence of the marker. With this type of system, however, reliability of the marker identification is relatively low due to the broad bandwidth of the simple resonant circuit. Moreover, the marker must be removed after identification, which is not desirable in such cases as antipilferage systems.

A second type of marker consists of a first elongated element of high magnetic permeability ferromagnetic material disposed adjacent to at least a second element of ferromagnetic material having higher coercivity than the first element. When subjected to an interrogation frequency of electromagnetic radiation, the marker generates harmonics of the interrogation frequency due to the non-linear characteristics of the marker. The detection of such harmonics in the receiving coil indicates the presence of the marker. Deactivation of the marker is accomplished by changing the state of magnetization of the second element, which can be easily achieved, for example, by passing the marker through a dc magnetic field. Harmonic marker systems are superior to the aforementioned radio-frequency resonant systems due to improved reliability of marker identification and simpler deactivation method. Two major problems, however, exist with this type of system: one is the difficulty of detecting the marker signal at remote distances. The amplitude of the harmonics generated by the marker is much smaller than the amplitude of the interrogation signal, limiting the detection aisle widths to less than about three feet. Another problem is the difficulty of distinguishing the marker signal from pseudo signals generated by other ferromagnetic objects such as belt buckles, pens, clips, etc.

Surveillance systems that employ detection modes incorporating the fundamental mechanical resonance frequency of the marker material are especially advantageous systems, in that they offer a combination of high detection sensitivity, high operating reliability, and low operating costs. Examples of such systems are disclosed in U.S. Patent Nos. 4,510,489 and 4,510,490 (hereinafter the '489 and '490 patents).

The marker in such systems is a strip, or a plurality of strips, of known length of a ferromagnetic material, packaged with a magnetically harder ferromagnet (material with a higher coercivity) that provides a biasing field to establish peak magneto-mechanical coupling. The ferromagnetic marker material is preferably a metallic glass alloy ribbon, since the efficiency of magneto-mechanical coupling in these alloys is very high. The mechanical resonance frequency of the marker material is dictated essentially by the length of the alloy ribbon and the biasing field strength. When an interrogating signal tuned to this resonance frequency is encountered, the marker material responds with a large signal field which is detected by the receiver. The large signal field is partially attributable to an enhanced magnetic permeability of the marker material at the resonance frequency. Various marker configurations and systems for the interrogation and detection that utilize the above principle have been taught in the '489 and '490 patents.

In one particularly useful system, the marker material is excited into oscillations by pulses, or bursts, of signal at its resonance frequency generated by the transmitter. When the exciting pulse is over, the marker material will undergo damped oscillations at its resonance frequency, i.e., the marker material "rings down" following the termination of the exciting pulse. The receiver "listens" to the response signal during this ring down period. Under this arrangement, the surveillance system is relatively immune to interference from various radiated or power line sources and, therefore, the potential for false alarms is essentially eliminated.

A broad range of alloys have been claimed in the '489 and '490 patents as suitable for marker material, for the various detection systems disclosed. Other metallic glass alloys bearing high permeability are disclosed in U.S. Patent No. 4,152,144.

A major problem in use of electronic article surveillance systems is the tendency for markers of surveillance systems based on mechanical resonance to accidentally trigger detection systems that are based an alternate technology, such as the harmonic marker systems described above: The non-linear magnetic response of the marker is strong enough to generate harmonics in the alternate system, thereby accidentally creating a pseudo response, or "false" alarm. The importance of avoiding interference among, or "pollution" of, different surveillance systems is readily apparent. Consequently, there exists a need in the art for a resonant marker that can be detected in a highly reliable manner without polluting systems based on alternate technologies, such as harmonic re-radiance.

SUMMARY OF INVENTION

The present invention provides magnetic alloys that are at least 70% glassy and, upon being annealed to enhance magnetic properties, are characterized by relatively linear magnetic responses in a frequency regime wherein harmonic marker systems operate magnetically. Such alloys can be cast into ribbon using rapid solidification, or otherwise formed into markers having magnetic and mechanical characteristics especially suited for use in surveillance systems based on magneto-mechanical actuation of the markers. Generally stated the glassy metal alloys of the present invention have a composition consisting essentially of the formula $Fe_a Co_b Ni_c M_d B_e Si_f C_g$, where M is selected from molybdenum, chromium and manganese and "a", "b", "c", "d", "e", "f" and "g" are in atom percent, "a" ranges from about 30 to about 45, "b" ranges from about 4 to about 40 and "c" ranges from about 5 to about 45, "d" ranges from about 0 to about 3,

"e" ranges from about 10 to about 25 , "f" ranges from about 0 to about 15 and "g" ranges from about 0 to about 2. Ribbons of these alloys, when mechanically resonant at frequencies ranging from about 48 to about 66 kHz, evidence relatively linear magnetization behavior up to an applied field of 8 Oe or more as well as the slope of resonant frequency versus bias field close to or exceeding the level of about 400 Hz/Oe exhibited by a conventional mechanical-resonant marker. Moreover, voltage amplitudes detected at the receiving coil of a typical resonant-marker system for the markers made from the alloys of the present invention are comparable to or higher than those of the existing resonant marker. These features assure that interference among systems based on mechanical resonance and harmonic re-radiance is avoided

The metallic glasses of this invention are especially suitable for use as the active elements in markers associated with article surveillance systems that employ excitation and detection of the magneto-mechanical resonance described above. Other uses may be found in sensors utilizing magneto-mechanical actuation and its related effects and in magnetic components requiring high magnetic permeability.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be more fully understood and further advantages will become apparent when reference is made to the following detailed description of the preferred embodiments of the invention and the accompanying drawings in which:

Fig. **1(a)** is a schematic representation of the magnetization curve taken along the length of a conventional resonant marker, where B is the magnetic induction and H is the applied magnetic field;

Fig. **1(b)** is a schematic representation of the magnetization curve taken along the length of the marker of the present invention, where H_a is a field above which B saturates;

Fig. 2 is a schematic representation of signal profile detected at the receiving coil depicting mechanical resonance excitation, termination of excitation at time t_o and subsequent ring-down, wherein V_o and V_1 are the signal amplitudes at the receiving coil at $t = t_o$ and $t = t_1$ (1 msec after t_o), respectively; and

Fig. 3 is a schematic representation of the mechanical resonance frequency, f_r , and response signal , V_1 , detected in the receiving coil at 1 msec after the termination of the exciting ac field as a function of the bias magnetic field, H_b, wherein H_{b1} and H_{b2} are the bias fields at which V_1 is a maximum and f_r is a minimum, respectively.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In accordance with the present invention, there are provided magnetic metallic glass alloys that are characterized by relatively linear magnetic responses in the frequency region where harmonic marker systems operate magnetically. Such alloys evidence all the features necessary to meet the requirements of markers for surveillance systems based on magneto-mechanical actuation. Generally stated the glassy metal alloys of the present invention have a composition consisting essentially of the formula $Fe_a Co_b Ni_c M_d B_e Si_f C_g$, where M is selected from molybdenum, chromium and manganese and "a", "b", "c", "d", "e", "f" and "g" are in atom percent, "a" ranges from about 30 to about 45, "b" ranges from about 4 to about 40 and "c" ranges from about 5 to about 45, "d" ranges from about 0 to about 3, "e" ranges from about 10 to about 25 , "f" ranges from about 0 to about 15 and "g" ranges from about 0 to about 2. The purity of the above compositions is that found in normal commercial practice. Ribbons of these alloys are annealed with a magnetic field applied across the width of the ribbons at elevated temperatures for a given period of time. Ribbon temperatures should be below its crystalization temperature and the ribbon, upon being heat treated, should be ductile enough to be cut up. The field strength during the annealing is such that

the ribbons saturate magnetically along the field direction. Annealing time depends on the annealing temperature and typically ranges from about a few minutes to a few hours. For commercial production, a continuous reel-to-reel annealing furace is preferred. In such cases, ribbon travelling speeds may be set at about between 0.5 and about 12 meter per minute. The annealed ribbons having, for example, a length of about 38 mm, exhibit relatively linear magnetic response for magnetic fields of up to 8 Oe or more applied parallel to the marker length direction and mechanical resonance in a range of frequencies from about 48 kHz to about 66 kHz. The linear magnetic response region extending to the level of 8 Oe is sufficient to avoid triggering some of the harmonic marker systems. For more stringent cases, the linear magnetic response region is extended beyond 8 Oe by changing the chemical composition of the alloy of the present invention. The annealed ribbons at lengths shorter or longer than 38 mm evidence higher or lower mechanical resonance frequencies than 48-66 kHz range.

Ribbons having mechanical resonance in the range from about 48 to 66 kHz are preferred. Such ribbons are short enough to be used as disposable marker materials. In addition, the resonance signals of such ribbons are well separated from the audio and commercial radio frequency ranges.

Most metallic glass alloys that are outside of the scope of this invention typically exhibit either non-linear magnetic response regions below 8 Oe level or H_a levels close to the operating magnetic excitation levels of many article detection systems utilizing harmonic markers. Resonant markers composed of these alloys accidentally trigger, and thereby pollute, many article detection systems of the harmonic re-radiance variety.

There are a few metallic glass alloys outside of the scope of this invention that do show linear magnetic response for an acceptable field range. These alloys, however, contain high levels of cobalt or molybdenum or chromium, resulting in increased raw material costs and/or reduced ribbon castability owing to the higher melting temperatures of such constituent elements as molybdenum or chromium.

The alloys of the present invention are advantageous, in that they afford, in combination, extended linear magnetic response, improved mechanical resonance performance, good ribbon castability and economy in production of usable ribbon.

Apart from the avoidance of the interference among different systems, the markers made from the alloys of the present invention generate larger signal amplitudes at the receiving coil than conventional mechanical resonant markers. This makes it possible to reduce either the size of the marker or increase the detection aisle widths, both of which are desirable features of article surveillance systems.

Examples of metallic glass alloys of the invention include $Fe_{40}Co_{34}Ni_{8}B_{13}Si_{5}$, $Fe_{40}Co_{30}Ni_{12}B_{13}Si_{5}$, $Fe_{40}Co_{26}Ni_{16}B_{13}Si_{5}$, $Fe_{40}Co_{22}Ni_{20}B_{13}Si_{5}$, $Fe_{40}Co_{20}Ni_{22}B_{13}Si_{5}$, $Fe_{40}Co_{18}Ni_{24}B_{13}Si_{5}$, $Fe_{35}Co_{18}Ni_{29}B_{13}Si_{5}$, $Fe_{32}Co_{18}Ni_{32}B_{13}Si_{5}$, $Fe_{40}Co_{16}Ni_{26}B_{13}Si_{5}$, $Fe_{40}Co_{14}Ni_{28}B_{13}Si_{5}$, $Fe_{40}Co_{14}Ni_{28}B_{16}Si_{2}$, $Fe_{40}Co_{14}Ni_{28}B_{11}Si_{7}$, $Fe_{40}Co_{14}Ni_{28}B_{13}Si_{3}C_{2}$, $Fe_{38}Co_{14}Ni_{30}B_{13}Si_{5}$, $Fe_{36}Co_{14}Ni_{32}B_{13}Si_{5}$, $Fe_{34}Co_{14}Ni_{34}B_{13}Si_{5}$, $Fe_{30}Co_{14}Ni_{38}B_{13}Si_{5}$, $Fe_{42}Co_{14}Ni_{26}B_{13}Si_{5}$, $Fe_{44}Co_{14}Ni_{24}B_{13}Si_{5}$, $Fe_{40}Co_{14}Ni_{27}Mo_{1}B_{13}Si_{5}$, $Fe_{40}Co_{14}Ni_{25}Mo_{3}B_{13}Si_{5}$, $Fe_{40}Co_{14}Ni_{27}Cr_{1}B_{13}Si_{5}$, $Fe_{40}Co_{14}Ni_{25}Cr_{3}B_{13}Si_{5}$, $Fe_{40}Co_{14}Ni_{25}Mo_{1}B_{13}Si_{5}C_{2}$, $Fe_{40}Co_{12}Ni_{30}B_{13}Si_{5}$, $Fe_{38}Co_{12}Ni_{32}B_{13}Si_{5}$, $Fe_{42}Co_{12}Ni_{30}B_{13}Si_{5}$, $Fe_{40}Co_{12}Ni_{26}B_{17}Si_{5}$, $Fe_{40}Co_{12}Ni_{28}B_{15}Si_{5}$, $Fe_{40}Co_{10}Ni_{32}B_{13}Si_{5}$, $Fe_{42}Co_{10}Ni_{30}B_{13}Si_{5}$, $Fe_{44}Co_{10}Ni_{28}B_{13}Si_{5}$, $Fe_{40}Co_{10}Ni_{31}Mo_{1}B_{13}Si_{5}$, $Fe_{40}Co_{10}Ni_{31}Cr_{1}B_{13}Si_{5}$, $Fe_{40}Co_{10}Ni_{31}Mn_{1}B_{13}Si_{5}$, $Fe_{40}Co_{10}Ni_{29}Mn_{3}B_{13}Si_{5}$, $Fe_{40}Co_{10}Ni_{30}B_{13}Si_{5}C_{2}$, $Fe_{40}Co_{8}Ni_{38}B_{13}Si_{5}$, $Fe_{40}Co_{6}Ni_{36}B_{13}Si_{5}$, and $Fe_{40}Co_{4}Ni_{38}B_{13}Si_{5}$, wherein subscripts are in atom percent.

The magnetization behavior characterized by a B-H curve is shown in Fig. 1 (a) for a conventional mechanical resonant marker, where B is the magnetic induction and H is the applied field. The overall B-H curve is sheared with a non-linear hysteresis loop existent in the low field region. This non-linear feature of the

marker results in higher harmonics generation, which triggers some of the harmonic marker systems, hence the interference among different article surveillance systems.

The definition of the linear magnetic response is given in Fig. 1 (b). As a marker is magnetized along the length direction by an external magnetic field, H, the magnetic induction, B, results in the marker. The magnetic response is relatively linear up to H_a, beyond which the marker saturates magnetically. The quantity H_a depends on the physical dimension of the marker and its magnetic anisotropy field. To prevent the resonant marker from accidentally triggering a surveillance system based on harmonic re-radiance, H_a should be above the operating field intensity region of the harmonic marker systems.

The marker material is exposed to a burst of exciting signal of constant amplitude, referred to as the exciting pulse, tuned to the frequency of mechanical resonance of the marker material. The marker material responds to the exciting pulse and generates output signal in the receiving coil following the curve leading to V_o in Fig. 2 . At time t_o , excitation is terminated and the marker starts to ring-down, reflected in the output signal which is reduced from V_o to zero over a period of time. At time t_1 , which is 1 msec after the termination of excitation, output signal is measured and denoted by the quantity V_1 . Thus V_1 / V_o is a measure of the ring-down. Although the principle of operation of the surveillance system is not dependent on the shape of the waves comprising the exciting pulse, the wave form of this signal is usually sinusoidal. The marker material resonates under this excitation.

The physical principle governing this resonance may be summarized as follows: When a ferromagnetic material is subjected to a magnetizing magnetic field, it experiences a change in length. The fractional change in length, over the original length, of the material is referred to as magnetostriction and denoted by the symbol λ. A positive signature is assigned to λ if an elongation occurs parallel to the magnetizing magnetic field.

When a ribbon of a material with a positive magnetostriction is subjected to a sinusoidally varying external field, applied along its length, the ribbon will undergo periodic changes in length, i.e., the ribbon will be driven into oscillations. The external field may be generated, for example, by a solenoid carrying a sinusoidally varying current. When the half-wave length of the oscillating wave of the ribbon matches the length of the ribbon, mechanical resonance results. The resonance frequency f_r is given by the relation

$$f_r = (1/2L)(E/D)^{0.5},$$

where L is the ribbon length, E is the Young's modulus of the ribbon, and D is the density of the ribbon.

Magnetostrictive effects are observed in a ferromagnetic material only when the magnetization of the material proceeds through magnetization rotation. No magnetostriction is observed when the magnetization process is through magnetic domain wall motion. Since the magnetic anisotropy of the marker of the alloy of the present invention is induced by field-annealing to be across the marker width direction, a dc magnetic field, referred to as bias field, applied along the marker length direction improves the efficiency of magneto-mechanical response from the marker material. It is also well understood in the art that a bias field serves to change the effective value for E, the Young's modulus, in a ferromagnetic material so that the mechanical resonance frequency of the material may be modified by a suitable choice of the bias field strength. The schematic representation of Fig. 3 explains the situation further: The resonance frequency, f_r, decreases with the bias field, H_b, reaching a minimum, $(f_r)_{min}$, at H_{b2}. The signal response, V_1, detected, say at $t = t_1$ at the receiving coil, increases with H_b, reaching a maximum, V_m, at H_{b1}. The slope, df_r/dH_b, near the operating bias field is an important quantity, since it related to the sensitivity of the surveillance system.

Summarizing the above, a ribbon of a positively magnetostrictive ferromagnetic material, when exposed to a driving ac magnetic field in the presence of a dc bias field, will oscillate at the frequency of the driving ac field, and when

this frequency coincides with the mechanical resonance frequency, f_r, of the material, the ribbon will resonate and provide increased response signal amplitudes. In practice, the bias field is provided by a ferromagnet with higher coercivity than the marker material present in the "marker package".

Table I lists typical values for V_m, H_{b1}, $(f_r)_{min}$ and H_{b2} for a conventional mechanical resonant marker based on glassy $Fe_{40} Ni_{38} Mo_4 B_{18}$. The low value of H_{b2}, in conjunction with the existence of the non-linear B-H bahavior below H_{b2}, tends to cause a marker based on this alloy to accidentally trigger some of the harmonic marker systems, resulting in interference among article surveillance systems based on mechanical resonance and harmonic re-radiance..

TABLE I

Typical values for V_m, H_{b1}, $(f_r)_{min}$ and H_{b2} for a conventional mechanical resonant marker based on glassy $Fe_{40} Ni_{38} Mo_4 B_{18}$. This ribbon at a length of 38.1 mm has mechanical resonance frequencies ranging from about 57 and 60 kHz.

V_m (mV)	H_{b1} (Oe)	$(f_r)_{min}$ (kHz)	H_{b2} (Oe)
150-250	4-6	57-58	5-7

Table II lists typical values for H_a, V_m, H_{b1}, $(f_r)_{min}$, H_{b2} and df_r/dH_b H_b for the alloys outside the scope of this patent. Field-annealing was performed in a continuous reel-to-reel furnace on 12.7 mm wide ribbon where ribbon speed was from about 0.6 m/min. to about 1.2 m/min.

TABLE II

Values for H_a, V_m, H_{b1}, $(f_r)_{min}$, H_{b2} and df_r/dH_b taken at H_b = 6 Oe for the alloys outside the scope of this patent. Field-annealing was performed in a continuous reel-to-reel furnace where ribbon speed was from about 0.6 m/min. to about 1.2 m/min with a magnetic field of about 1.4 kOe applied perpendicular to the ribbon length direction.

Composition (at.%)	H_a (Oe)	V_m (mV)	H_{b1} (Oe)	$(f_r)_{min}$ (kHz)	H_{b2} (Oe)	df_r/dH_b (Hz/Oe)
A. $Co_{42}Fe_{40}B_{13}Si_5$	22	400	7.0	49.7	15.2	700
B. $Co_{38}Fe_{40}Ni_4B_{13}Si_5$	20	420	9.3	53.8	16.4	500
C. $Co_2Fe_{40}Ni_{40}B_{13}Si_5$	10	400	3.0	50.2	6.8	2,080
D. $Co_{10}Fe_{40}Ni_{27}Mn_5B_{13}Si_5$	7.5	400	2.7	50.5	6.8	2,300

Although alloys A and B show linear magnetic responses for acceptable magnetic field ranges, but contain high levels of cobalt, resulting in increased raw material costs. Alloys C and D have low H_{b1} values and high df_r/dH_b values, combination of which are not desirable from the standpoint of resonant marker system operation.

EXAMPLES

Example 1: Fe-Co-Ni-B-Si metallic glasses

1. Sample Preparation

Glassy metal alloys in the Fe-Co-Ni-B-Si series, designated as samples No. 1 to 29 in Table III and IV, were rapidly quenched from the melt following the techniques taught by Narasimhan in U.S. Patent No. 4,142,571, the disclosure of

which is hereby incorporated by reference thereto. All casts were made in an inert gas, using 100 g melts. The resulting ribbons, typically 25 μm thick and about 12.7 mm wide, were determined to be free of significant crystallinity by x-ray diffractometry using Cu-Kα radiation and differential scanning calorimetry. Each of the alloys was at least 70 % glassy and, in many instances, the alloys were more than 90 % glassy. Ribbons of these glassy metal alloys were strong, shiny, hard and ductile.

The ribbons were cut into small pieces for magnetization, magnetostriction, Curie and crystallization temperature and density measurements. The ribbons for magneto-mechanical resonance characterization were cut to a length of about 38.1 mm and were heat treated with a magnetic field applied across the width of the ribbons. The strength of the magnetic field was 1.1 kOe or 1.4 kOe and its direction was varied between 75° and 90° with respect to the ribbon length direction. Some of the ribbons were heat-treated under tension ranging from about zero to 7.2 kg/mm^2 applied along the direction of the ribbon. The speed of the ribbon in the reel-to-reel annealing furnace was changed from about 0.5 meter per minute to about 12 meter per minute.

2. Characterization of magnetic and thermal properties

Table III lists saturation induction (B_s), saturation magnetostriction (λ_s), and crystallization (T_c) temperature of the alloys. Magnetization was measured by a vibrating sample magnetometer, giving the saturation magnetization value in emu/g which is converted to the saturation induction using density data. Saturation magnetostriction was measured by a strain-gauge method, giving in 10^{-6} or in ppm. Curie and crystallization temperatures were measured by an inductance method and a differential scanning calorimetry, respectively.

TABLE III

Magnetic and thermal properties of Fe-Co-Ni-B-Si glassy alloys. Curie temperatures of alloy No. 22 (θ_f =447 ° C), No. 27 (θ_f =430 ° C), No. 28 (θ_f =400 ° C) and 29 (θ_f =417 ° C) could be determined because they are below the first crystallization temperatures (T_c).

No.	Composition (at.%)					B_s (Tesla)	λ_s (ppm)	T_c (°C)
	Fe	Co	Ni	B	Si			
1	40	34	8	13	5	1.46	23	456
2	40	30	12	13	5	1.42	22	455
3	40	26	16	13	5	1.38	22	450
4	40	22	20	13	5	1.32	20	458
5	40	20	22	13	5	1.28	19	452
6	40	18	24	13	5	1.25	20	449
7	35	18	29	13	5	1.17	17	441
8	32	18	32	13	5	1.07	13	435
9	40	16	26	13	5	1.21	18	448
10	40	14	28	13	5	1.22	19	444
11	40	14	28	16	2	1.25	19	441
12	40	14	28	11	7	1.20	15	444
13	38	14	30	13	5	1.19	18	441
14	36	14	32	13	5	1.14	17	437
15	34	14	34	13	5	1.09	17	434
16	30	14	38	13	5	1.00	10	426
17	42	14	26	13	5	1.27	21	448
18	44	14	24	13	5	1.31	21	453
19	40	12	30	13	5	1.20	18	442
20	38	12	32	13	5	1.14	18	440
21	42	12	30	13	3	1.29	21	415
22	40	12	26	17	5	1.12	17	498
23	40	12	28	15	5	1.20	19	480
24	40	10	32	13	5	1.16	17	439
25	42	10	30	13	5	1.15	19	443
26	44	10	28	13	5	1.25	20	446
27	40	8	34	13	5	1.11	17	437
28	40	6	36	13	5	1.12	17	433
29	40	4	38	13	5	1.09	17	430

Each marker material having a dimension of about 38.1mmx12.7mmx20μm was tested by a conventional B-H loop tracer to measure the quantity of H_a and then was placed in a sensing coil with 221 turns. An ac magnetic field was applied along the longitudinal direction of each alloy marker with a dc bias field changing from 0 to about 20 Oe. The sensing coil detected the magneto-mechanical response of the alloy marker to the ac excitation. These marker materials mechanically resonate between about 48 and 66 kHz. The quantities characterizing the magneto-mechanical response were measured and are listed in Table IV for the alloys listed in Table III.

TABLE IV

Values of H_a, V_m, H_{b1}, $(f_r)_{min}$, H_{b2} and df_r/dH_b taken at H_b = 6 Oe for the alloys of Table III heat-treated at 380 °C in a continuous reel-to-reel furnace with a ribbon steed of about 1.2 m/minute and at 415 °C for 30 min (indicated by asterisks *). The annealing field was about 1.4 kOe applied perpendicular to the ribbon length direction.

Alloy No.	H_a (Oe)	V_m (mV)	H_{b1} (Oe)	$(f_r)_{min}$ (kHz)	H_{b2} (Oe)	df_r/dH_b (Hz/Oe)
1	21	415	10.3	54.2	16.5	460
2	20	370	10.7	54.2	16.0	560
3	20	370	10.0	53.8	16.5	430
4*	20	250	10.5	49.8	17.7	450
4	18	330	8.0	53.6	14.2	590
5	17	270	9.0	52.0	14.5	710
6	17	340	7.8	53.4	14.2	620
7	16	300	8.6	53.5	14.3	550
8	15	380	8.0	54.1	13.0	580

9	16	450	7.8	51.3	14.2	880
10*	17	390	8.9	49.3	15.9	550
10	16	390	7.0	52.3	13.4	810
11	15	350	8.0	52.3	13.9	750
12	14	350	7.0	52.5	12.4	830
13	14	400	7.3	52.5	13.1	780
14	13	330	6.5	54.2	12.6	670
15	13	270	6.2	53.0	11.5	820
16	10	230	5.0	56.0	9.3	1430
17	15	415	7.2	51.2	14.3	740
18	15	350	7.7	50.4	12.9	1080
19	14	440	6.5	50.6	11.6	960
20	14	330	6.6	52.9	11.3	900
21	19	325	9.3	53.9	14.8	490
22	9	260	3.5	55.8	8.0	1700
23	11	310	5.4	52.2	10.5	1380
24*	15	220	8.2	48.5	13.7	740
24	14	410	7.5	51.8	13.5	800
25	13	420	6.2	49.5	12.2	1270
26	14	400	6.0	50.2	12.8	1050
27	10	250	4.0	51.9	8.5	1490
28	12	440	4.0	49.7	9.0	1790
29	11	380	5.2	51.5	9.8	1220

All the alloys listed in Table IV exhibit H_a values exceeding 8 Oe, which make them possible to avoid the interference problem mentioned above. Good sensitivity (df_r/dH_b) and large response signal (V_m) result in smaller markers for resonant marker systems.

The quantities characterizing the magneto-mechanical resonance of the marker material of Table III heat-treated under different annealing conditions are summarized in Tables V, VI, VII, VIII and IX.

TABLE V

Values of V_m, H_{b1}, $(f_r)_{min}$, df_r/dH_b taken at $H_b = 6$ Oe for alloy No. 8 of Table III heat-treated under different conditions in a reel-to-reel annealing furnace. Applied field direction indicated is the angle btween the ribbon length direction and the field direction.

Annealing Temperature: 440 ° C Applied Field/Direction: 1.1 kOe / 90 °

Ribbon Speed (m/minute)	Tension (kg/mm²)	V_m (mV)	H_m (Oe)	$(f_r)_{min}$ (kHz)	H_{b2} (Oe)	df_r/dH_b (Hz/Oe)
9.0	1.4	360	3.9	55.3	8.5	590
10.5	1.4	340	3.8	55.4	8.5	540
10.5	6.0	225	5.0	55.8	9.8	690

Annealing Temperature: 400° C Applied Field/Direction: 1.1 kOe / 90 °

Ribbon Speed (m/minute)	Tension (kg/mm²)	V_m (mV)	H_m (Oe)	$(f_r)_{min}$ (kHz)	H_{b2} (Oe)	df_r/dH_b (Hz/Oe)
9.0	0	300	4.1	53.7	8.3	1170
9.0	7.2	250	5.2	55.9	9.7	

Annealing Temperature: 340 ° C Applied Field Direction: 1.1 kOe / 75 °

Ribbon Speed (m/minute)	Tension (kg/mm²)	V_m (mV)	H_m (Oe)	$(f_r)_{min}$ (kHz)	H_{b2} (Oe)	df_r/dH_b (Hz/Oe)
0.6	0	315	7.9	55.7	13.4	420
2.1	0	225	8.0	56.1	12.8	470

TABLE VI

Values of V_m, H_{b1}, $(f_r)_{min}$, df_r/dH_b taken at H_b = 6 Oe for alloy No. 17 of Table III heat-treated under different conditions in a reel-to-reel annealing furnace. Applied field direction indicated is the angle btween the ribbon length direction and the field direction.

Annealing Temperature: 320 ° C Applied Field/Direction: 1.4 kOe / 90 °

Ribbon Speed (m/minute)	Tension (kg/mm²)	V_m (mV)	H_m (Oe)	$(f_r)_{min}$ (kHz)	H_{b2} (Oe)	df_r/dH_b (Hz/Oe)
0.6	0	250	6.0	55.3	13.0	670
0.6	1.4	320	6.0	54.0	14.1	620
0.6	3.6	370	7.0	52.2	14.0	630

Annealing Temperature: 280 ° C Applied Field/Direction: 1.1 kOe / 90 °

Ribbon Speed (m/minute)	Tension (kg/mm²)	V_m (mV)	H_m (Oe)	$(f_r)_{min}$ (kHz)	H_{b2} (Oe)	df_r/dH_b (Hz/Oe)
0.6	7.2	390	7.0	53.2	13.9	615
2.1	7.2	240	5.0	53.6	11.5	760

Annealing Temperature: 280 ° C Applied Field/Direction: 1.1 kOe / 75 °

Ribbon Speed (m/minute)	Tension (kg/mm²)	V_m (mV)	H_m (Oe)	$(f_r)_{min}$ (kHz)	H_{b2} (Oe)	df_r/dH_b (Hz/Oe)
0.6	7.2	360	6.3	52.9	13.2	630
2.1	7.2	270	5.2	53.2	11.2	860

TABLE VII

Values of V_m, H_{b1}, $(f_r)_{min}$, df_r/dH_b taken at H_b = 6 Oe for alloy No. 24 of Table III heat-treated under different conditions in a reel-to-reel annealing furnace. Applied field direction indicated is the angle btween the ribbon length direction and the field direction.

Annealing Temperature: 320 ° C   Applied Field/Direction: 1.1 kOe / 90 °

Ribbon Speed (m/minute)	Tension (kg/mm^2)	V_m (mV)	H_m (Oe)	$(f_r)_{min}$ (kHz)	H_{b2} (Oe)	df_r / dH_b (Hz/Oe)
0.6	0	280	8.0	54.7	13.1	450
2.1	0	310	7.6	54.7	12.0	500
2.1	7.2	275	8.0	55.1	14.5	450

Annealing Temperature: 320 ° C   Applied Field/Direction: 1.1 kOe / 75 °

Ribbon Speed (m/minute)	Tension (kg/mm^2)	V_m (mV)	H_m (Oe)	$(f_r)_{min}$ (kHz)	H_{b2} (Oe)	df_r / dH_b (Hz/Oe)
0.6	0	310	8.2	54.7	13.0	530
0.6	7.2	275	8.2	55.2	15.0	430
2.1	0	290	7.2	54.8	12.0	550
2.1	7.2	270	7.0	55.6	13.5	480

Annealing Temperature: 300 ° C   Applied Field/Direction: 1.1 kOe / 82.5 °

Ribbon Speed (m/minute)	Tension (kg/mm^2)	V_m (mV)	H_m (Oe)	$(f_r)_{min}$ (kHz)	H_{b2} (Oe)	df_r / dH_b (Hz/Oe)
0.6	2.1	300	8.3	54.9	13.7	410
2.1	2.1	300	7.0	54.4	11.8	480

Annealing Temperature: 280 ° C   Applied Field/Direction: 1.1 kOe / 90 °

Ribbon Speed (m/minute)	Tension (kg/mm^2)	V_m (mV)	H_m (Oe)	$(f_r)_{min}$ (kHz)	H_{b2} (Oe)	df_r / dH_b (Hz/Oe)
0.6	0	265	8.4	55.2	12.6	430
2.1	7.2	255	6.8	55.9	12.0	490

TABLE VIII

Values of V_m, H_{b1}, $(f_r)_{min}$, df_r / dH_b taken at H_b = 6 Oe for alloy No. 27 of Table III heat-treated under different conditions in a reel-to-reel annealing furnace. Applied field direction indicated is the angle btween the ribbon length direction and the field direction.

Annealing Temperature: 300 ° C   Applied Field/Direction: 1.1 kOe / 82.5 °

Ribbon Speed (m/minute)	Tension (kg/mm^2)	V_m (mV)	H_m (Oe)	$(f_r)_{min}$ (kHz)	H_{b2} (Oe)	df_r / dH_b (Hz/Oe)
0.6	2.1	270	6.2	53.8	11.9	690
2.1	2.1	270	5.2	52.9	10.5	870

Annealing Temperature: 280 ° C   Applied Field/Direction: 1.1 kOe / 90 °

Ribbon Speed (m/minute)	Tension (kg/mm^2)	V_m (mV)	H_m (Oe)	$(f_r)_{min}$ (kHz)	H_{b2} (Oe)	df_r / dH_b (Hz/Oe)
0.6	7.2	290	5.8	53.8	12.0	670
2.1	0	230	6.0	54.3	11.0	720

TABLE IX

Values of V_m, H_{b1}, $(f_r)_{min}$, df_r/dH_b taken at H_b = 6 Oe for alloy No. 29 of Table III heat-treated under different conditions in a reel-to-reel annealing furnace. Applied field direction indicated is the angle btween the ribbon length direction and the field direction.

Annealing Temperature: 320 ° C   Applied Field/Direction: 1.1 kOe / 90 °

Ribbon Speed (m/minute)	Tension (kg/mm^2)	V_m (mV)	H_m (Oe)	$(f_r)_{min}$ (kHz)	H_{b2} (Oe)	df_r/dH_b (Hz/Oe)
2.1	7.2	225	4.7	55.2	10.0	570

Annealing Temperature: 280 ° C   Applied Field/Direction: 1.1 kOe / 75 °

Ribbon Speed (m/minute)	Tension (kg/mm^2)	V_m (mV)	H_m (Oe)	$(f_r)_{min}$ (kHz)	H_{b2} (Oe)	df_r/dH_b (Hz/Oe)
0.6	0	230	5.8	54.2	11.0	720
0.6	7.2	245	5.2	54.7	11.2	620

Above tables indicate that desired performance of a magneto-mechanical resonant marker can be achieved by proper combination of alloy chemistry and heat-treatment conditions.

Example 2: Fe-Co-Ni-Mo/Cr/Mn-B-Si-C metallic glasses

Glassy metal alloys in the Fe-Co-Ni-Mo/Cr/Mn-B-Si-C system were prepared and characterized as detailed under Example 1. Table X lists chemical compositions, magnetic and thermal properties and Table XI lists quantities characterizing mechanical resonance responses of the alloys of Table X.

TABLE X

Magnetic and thermal properties of low cobalt containing glassy alloys. T_c is the first crystallization temperature.

Alloy No.	Fe	Co	Ni	Mo	Cr	Mn	B	Si	C	B_s (Tesla)	λ_s (ppm)	T_c (°C)
1	40	14	28	-	-	-	13	3	2	1.22	19	441
2	40	14	27	1	-	-	13	5	-	1.18	18	451
3	40	14	25	3	-	-	13	5	-	1.07	13	462
4	40	14	27	-	1	-	13	5	-	1.18	20	462
5	40	14	25	-	3	-	13	5	-	1.07	15	451
6	40	14	25	1	-	-	13	5	2	1.15	15	480
7	40	10	31	1	-	-	13	5	-	1.12	18	447
8	40	10	31	-	1	-	13	5	-	1.13	18	441
9	40	10	31	-	-	1	13	5	-	1.16	18	445
10	40	10	29	-	-	3	13	5	-	1.19	17	454
11	40	10	30	-	-	-	13	5	2	1.13	16	465

TABLE XI

Values of H_a, V_m, H_{b1}, $(f_r)_{min}$, H_{b2} and df_r/dH_b taken at H_b = 6 Oe for the alloys listed in Table X heat-treated at 380 °C in a continuous reel-to-reel furnace with a ribbon speed of about 0.6 m/minute with a field of 1.4 kOe applied across the ribbon width.

Alloy No.	H_a (Oe)	V_m (mV)	H_{b1} (Oe)	$(f_r)_{min}$ (kHz)	H_{b2} (Oe)	df_r/dH_b (Hz/Oe)
1	14	310	8.3	52.5	13.1	870

2	13	350	4.4	51.7	10.0	1640
3	12	250	3.0	51.7	6,4	1790
4	11	320	6.2	51.8	9.8	950
5	10	480	3.7	51.5	8.2	1780
6	9	390	4.1	52.0	8.5	1820
7	10	460	4.2	50.3	8.9	1730
8	10	480	5.2	51.6	9.8	1560
9	12	250	6.5	51.2	10.6	1000
10	10	380	3.5	51.0	7.8	1880
11	9	310	4.0	51.5	8.0	1880

All the alloys listed in Table XI exhibit H_a values exceeding 8 Oe, which make them possible to avoid the interference problems mentioned above. Good sensitivity (df_r/dH_b) and large magneto-mechanical resonance response signal (V_m) result in smaller markers for resonant marker systems.

Having thus described the invention in rather full detail, it will be understood that such detail need not be strictly adhered to but that further changes and modifications may suggest themselves to one skilled in the art, all falling within the scope of the invention as defined by the subjoined claims.

What is claimed is:

1. A magnetic metallic glass alloy that is at least about 70% glassy, has been annealed to enhance magnetic properties, and has a composition consisting essentially of the formula $Fe_a Co_b Ni_c M_d B_e Si_f C_g$,where M is at least one member selected from the group consisting of molybdenum , chromium and manganese, "a", "b", "c", "d", "e", "f" and "g" are in atom percent, "a" ranges from about 30 to about 45, "b" ranges from about 4 to about 40 and "c" ranges from about 5 to about 45, "d" ranges from about 0 to about 3, "e" ranges from about 10 to about 25 , "f" ranges from about 0 to about 15 and "g" ranges from about 0 to about 2.

2. An alloy as recited by claim 1, having the form of a heat-treated strip that exhibits mechanical resonance in a range of frequencies from about 48 kHz to about 66 kHz, and having a relatively linear magnetization behavior up to a minimum bias field of about 8 Oe.

3. An alloy as recited by claim 2, wherein the slope of the mechanical resonance frequency versus bias field at about 6 Oe is close to or exceeds about 400 Hz/Oe.

4. An alloy as recited by claim 2, wherein the bias field at which the mechanical resonance frequency takes a minimum is close to or exceeds about 8 Oe.

5. An alloy'as recited by claim 2, wherein M is molybdenum.

6. An alloy as recited by claim 2, wherein M is chromium.

7. An alloy as recited by claim 2, wherein M is manganese.

8. An alloy as recited by claim 2, wherein "a" ranges from about 30 to about 45, the sum of "b" plus "c" ranges from about 32 to about 47, and the sum of "e" plus "f" plus "g" ranges from about 16 to about 22.

9. A magnetic alloy as recited by claim 8, having a composition selected from the group consisting of $Fe_{40}Co_{34}Ni_{8}B_{13}Si_{5}$, $Fe_{40}Co_{30}Ni_{12}B_{13}Si_{5}$, $Fe_{40}Co_{26}Ni_{16}B_{13}Si_{5}$, $Fe_{40}Co_{22}Ni_{20}B_{13}Si_{5}$, $Fe_{40}Co_{20}Ni_{22}B_{13}Si_{5}$, $Fe_{40}Co_{18}Ni_{24}B_{13}Si_{5}$, $Fe_{35}Co_{18}Ni_{29}B_{13}Si_{5}$, $Fe_{32}Co_{18}Ni_{32}B_{13}Si_{5}$, $Fe_{40}Co_{16}Ni_{26}B_{13}Si_{5}$, $Fe_{40}Co_{14}Ni_{28}B_{13}Si_{5}$, $Fe_{40}Co_{14}Ni_{28}B_{16}Si_{2}$, $Fe_{40}Co_{14}Ni_{28}B_{11}Si_{7}$, $Fe_{40}Co_{14}Ni_{28}B_{13}Si_{3}C_{2}$, $Fe_{38}Co_{14}Ni_{30}B_{13}Si_{5}$, $Fe_{36}Co_{14}Ni_{32}B_{13}Si_{5}$, $Fe_{34}Co_{14}Ni_{34}B_{13}Si_{5}$, $Fe_{30}Co_{14}Ni_{38}B_{13}Si_{5}$, $Fe_{42}Co_{14}Ni_{26}B_{13}Si_{5}$, $Fe_{44}Co_{14}Ni_{24}B_{13}Si_{5}$, $Fe_{40}Co_{14}Ni_{27}Mo_{1}B_{13}Si_{5}$, $Fe_{40}Co_{14}Ni_{25}Mo_{3}B_{13}Si_{5}$, $Fe_{40}Co_{14}Ni_{27}Cr_{1}B_{13}Si_{5}$, $Fe_{40}Co_{14}Ni_{25}Cr_{3}B_{13}Si_{5}$, $Fe_{40}Co_{14}Ni_{25}Mo_{1}B_{13}Si_{5}C_{2}$, $Fe_{40}Co_{12}Ni_{30}B_{13}Si_{5}$, $Fe_{38}Co_{12}Ni_{32}B_{13}Si_{5}$, $Fe_{42}Co_{12}Ni_{30}B_{13}Si_{5}$, $Fe_{40}Co_{12}Ni_{26}B_{17}Si_{5}$, $Fe_{40}Co_{12}Ni_{28}B_{15}Si_{5}$, $Fe_{40}Co_{10}Ni_{32}B_{13}Si_{5}$, $Fe_{42}Co_{10}Ni_{30}B_{13}Si_{5}$, $Fe_{44}Co_{10}Ni_{28}B_{13}Si_{5}$, $Fe_{40}Co_{10}Ni_{31}Mo_{1}B_{13}Si_{5}$, $Fe_{40}Co_{10}Ni_{31}Cr_{1}B_{13}Si_{5}$, $Fe_{40}Co_{10}Ni_{31}Mn_{1}B_{13}Si_{5}$, $Fe_{40}Co_{10}Ni_{29}Mn_{3}B_{13}Si_{5}$, $Fe_{40}Co_{10}Ni_{30}B_{13}Si_{5}C_{2}$, $Fe_{40}Co_{8}Ni_{38}B_{13}Si_{5}$, $Fe_{40}Co_{6}Ni_{36}B_{13}Si_{5}$, and $Fe_{40}Co_{4}Ni_{38}B_{13}Si_{5}$, wherein subscripts are in atom percent.

10. In an article surveillance system adapted to detect a signal produced by mechanical resonance of a marker within an applied magnetic field, the improvement wherein said marker comprises at least one strip of ferromagnetic material that is at least about 70 % glassy, has been annealed to enhance magnetic properties and has a composition consisting essentially of the formula $Fe_{a}Co_{b}Ni_{c}M_{d}B_{e}Si_{f}C_{g}$, where M at least one member selected from the group consisting of

molybdenum , chromium and manganese, "a", "b", "c", "d", "e", "f" and "g" are in atom percent, "a" ranges from about 30 to about 45, "b" ranges from about 4 to about 40, "c" ranges from about 5 to about 45, "d" ranges from about 0 to about 3, "e" ranges from about 10 to about 25, "f" ranges from about 0 to about 15 and "g" ranges from about 0 to about 2.

11. An article surveillance system as recited by claim 10, wherein said strip is selected from the group consisting of ribbon, wire and sheet.

12. An article surveillance system as recited by claim 11, wherein said strip is a ribbon.

13. An article surveillance system as recited by claim 10, wherein said strip exhibits mechanical resonance in a range of frequencies from about 48 kHz to about 66 kHz, and a relatively linear magnetization behavior up to a bias field of at least 8 Oe.

14. An article surveillance system as recited by claim 13, wherein the slope of the mechanical resonance frequency versus bias field for said strip at about 6 Oe is close to or exceeds about 400 Hz/Oe.

15. An article surveillance system as recited by claim 13, wherein the bias field at which the mechanical resonance frequency of said strip takes a minimum is close to or exceeds about 8 Oe.

16. An article surveillance system as recited by claim 13, wherein M is molybdenum.

17. An article surveillance system as recited by claim 13, wherein M is the element chromium.

18. An article surveillance system as recited by claim 15, wherein M is the element manganese.

19. An article surveillance system as recited by claim 13, wherein "a" ranges from about 30 to about 45, the sum of "b" plus "c" ranges from about 32 to about 47, and the sum of "e" plus "f" plus "g" ranges from about 16 to about 22.

20. An article surveillance system as recited by claim 23, wherein said strip has a composition selected from the group consisting of $Fe_{40}Co_{34}Ni_{8}B_{13}Si_{5}$, $Fe_{40}Co_{30}Ni_{12}B_{13}Si_{5}$, $Fe_{40}Co_{26}Ni_{16}B_{13}Si_{5}$, $Fe_{40}Co_{22}Ni_{20}B_{13}Si_{5}$, $Fe_{40}Co_{20}Ni_{22}B_{13}Si_{5}$, $Fe_{40}Co_{18}Ni_{24}B_{13}Si_{5}$, $Fe_{35}Co_{18}Ni_{29}B_{13}Si_{5}$, $Fe_{32}Co_{18}Ni_{32}B_{13}Si_{5}$, $Fe_{40}Co_{16}Ni_{26}B_{13}Si_{5}$, $Fe_{40}Co_{14}Ni_{28}B_{13}Si_{5}$, $Fe_{40}Co_{14}Ni_{28}B_{16}Si_{2}$, $Fe_{40}Co_{14}Ni_{28}B_{11}Si_{7}$, $Fe_{40}Co_{14}Ni_{28}B_{13}Si_{3}C_{2}$, $Fe_{38}Co_{14}Ni_{30}B_{13}Si_{5}$, $Fe_{36}Co_{14}Ni_{32}B_{13}Si_{5}$, $Fe_{34}Co_{14}Ni_{34}B_{13}Si_{5}$, $Fe_{30}Co_{14}Ni_{38}B_{13}Si_{5}$, $Fe_{42}Co_{14}Ni_{26}B_{13}Si_{5}$, $Fe_{44}Co_{14}Ni_{24}B_{13}Si_{5}$, $Fe_{40}Co_{14}Ni_{27}Mo_{1}B_{13}Si_{5}$, $Fe_{40}Co_{14}Ni_{25}Mo_{3}B_{13}Si_{5}$, $Fe_{40}Co_{14}Ni_{27}Cr_{1}B_{13}Si_{5}$, $Fe_{40}Co_{14}Ni_{25}Cr_{3}B_{13}Si_{5}$, $Fe_{40}Co_{14}Ni_{25}Mo_{1}B_{13}Si_{5}C_{2}$, $Fe_{40}Co_{12}Ni_{30}B_{13}Si_{5}$, $Fe_{38}Co_{12}Ni_{32}B_{13}Si_{5}$, $Fe_{42}Co_{12}Ni_{30}B_{13}Si_{5}$, $Fe_{40}Co_{12}Ni_{26}B_{17}Si_{5}$, $Fe_{40}Co_{12}Ni_{28}B_{15}Si_{5}$, $Fe_{40}Co_{10}Ni_{32}B_{13}Si_{5}$, $Fe_{42}Co_{10}Ni_{30}B_{13}Si_{5}$, $Fe_{44}Co_{10}Ni_{28}B_{13}Si_{5}$, $Fe_{40}Co_{10}Ni_{31}Mo_{1}B_{13}Si_{5}$, $Fe_{40}Co_{10}Ni_{31}Cr_{1}B_{13}Si_{5}$, $Fe_{40}Co_{10}Ni_{31}Mn_{1}B_{13}Si_{5}$, $Fe_{40}Co_{10}Ni_{29}Mn_{3}B_{13}Si_{5}$, $Fe_{40}Co_{10}Ni_{30}B_{13}Si_{5}C_{2}$, $Fe_{40}Co_{8}Ni_{38}B_{13}Si_{5}$, $Fe_{40}Co_{6}Ni_{36}B_{13}Si_{5}$, and $Fe_{40}Co_{4}Ni_{38}B_{13}Si_{5}$, wherein subscripts are in atom percent.

21. An alloy as recited by claim 2, having been heat-treated with a magnetic field.

22. An alloy as recited in claim 21, wherein said magnetic field is applied at a field strength such that said strip saturates magnetically along the field direction.

23. An alloy as recited in claim 22, wherein said strip has a length direction and said magnetic field is applied across siad strip width direction, the direction of said magnetic field ranging from about 75 ° to about 90 ° with respect to the strip length direction.

24. An alloy as recited by claim 23, wherein said magnetic field has a magnitude ranging from about 1 to about 1.5 kOe.

25. An alloy as recited by claim 23, wherein said heat-treatment step is carried out for a time period ranging from a few minues to a few hours at a temperature below the alloy's crystallization temperature.

26. An alloy recited by claim 2, wherein said heat-treatment is carried out in a continuous reel-to-reel furnace, said magnetic field has a magnitude ranging from about 1 to 1.5 kOe applied across said strip width rection making an angle ranging from about 75 ° to about 90 ° with respect to said strip length direction and said strip has a width ranging from about one millimeter to about 15 mm and a speed ranging from about 0.5 m/min. to about 12 m/min. and is under a tension ranging from about zero to about 7.2 kg/mm^2. the temperature of said heat-treatment being determined such that the temperature of said strip is below its crystallization temperature and said strip, upon being heat-treated, is ductile enough to be cut.

FIG. 1a

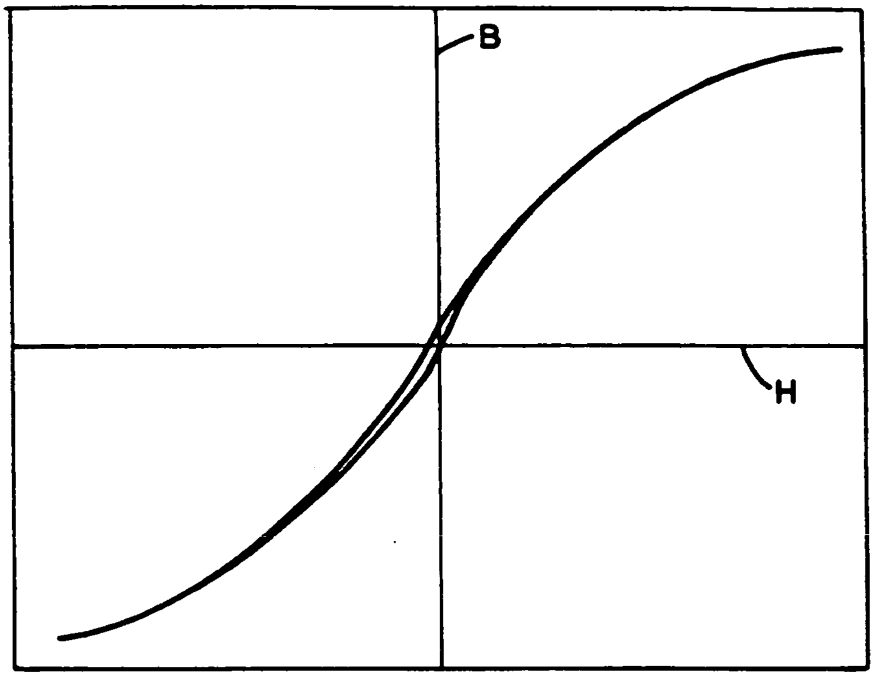
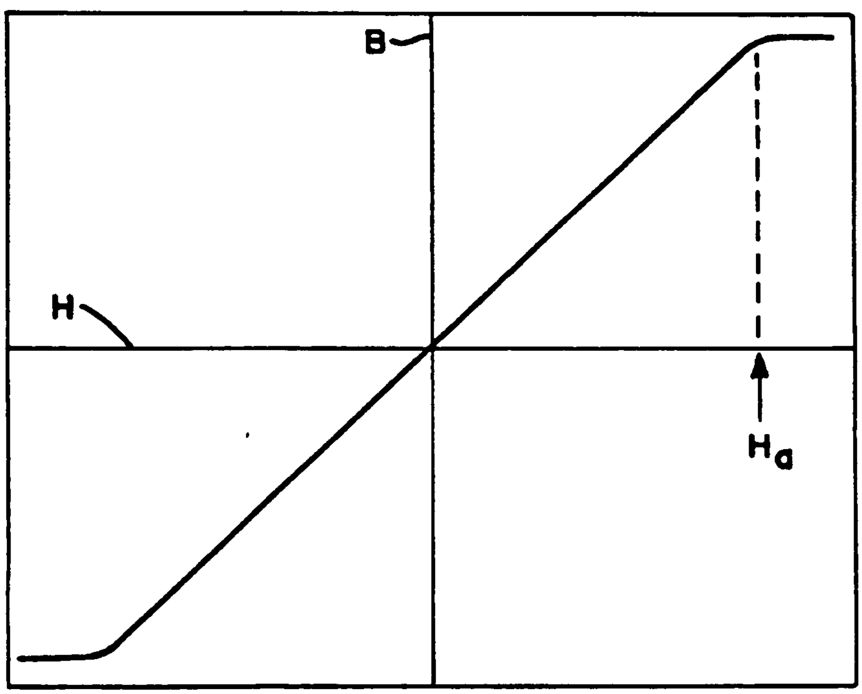
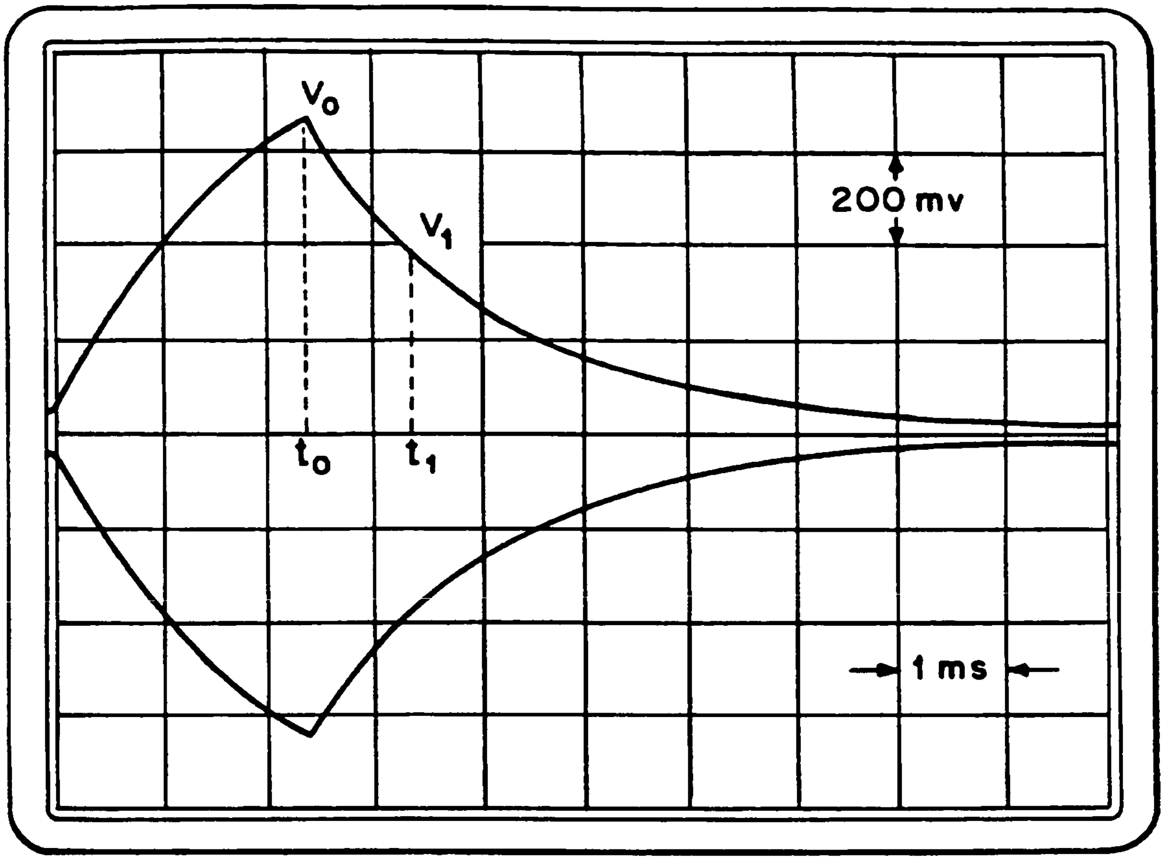


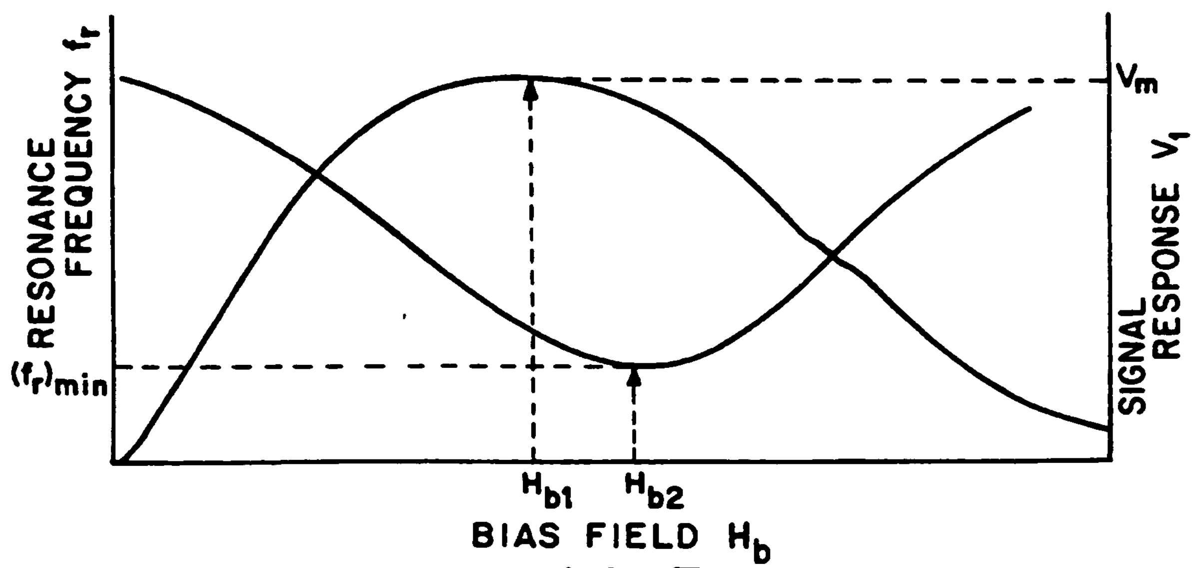
FIG. 1b





V_0
V_1
200 mv
t_0
t_1
1 ms

FIG. 2



RESONANCE FREQUENCY f_r
$(f_r)_{min}$
V_m
SIGNAL RESPONSE V_1
H_{b1}
H_{b2}
BIAS FIELD H_b

FIG. 3

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/05093

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C22C45/00 H01F1/153

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C22C H01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A,4 484 184 (GREGOR ET AL.) 20 November 1984 see the whole document ---	1,5,6
Y	EP,A,0 342 922 (K.K.TOSHIBA) 23 November 1989 see claims 1-7 ---	1,5,6
P,Y	EP,A,0 651 068 (UNITIKA LTD.) 3 May 1995 see the whole document ---	1
A	EP,A,0 072 893 (ALLIED CORPORATION) 2 March 1983 see claims 1-5 ---	1-9
A	DE,A,30 21 224 (SONY CORP.) 18 December 1980 see claims 1-3 -----	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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"P" document published prior to the international filing date but later than the priority date claimed

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"&" document member of the same patent family

1

Date of the actual completion of the international search	Date of mailing of the international search report
25 July 1996	06.08.96

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Lippens, M

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 96/05093

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